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Structure and Properties of Energetic Materials

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Structure and Properties of Energetic Materials

Symposium held November 30-December 2, 1992, Boston, Massachusetts, U.S.A.

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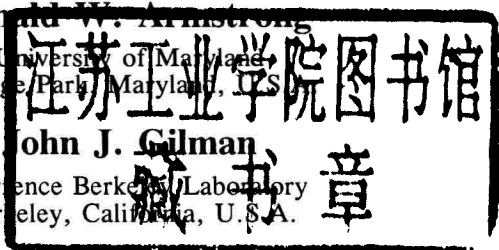
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Structure and Properties of Energetic Materials

Preface

This was the first Symposium on Energetic Materials held at a Materials Research Society Meeting. Energetic materials are substances that undergo exothermic chemical reaction in response to some stimulus and react in time scales leading to combustion, explosion, and/or detonation (millisec to femtosec). Energetic materials represent a multibillion dollar industry for both commercial and military uses. These are among the earliest of man-made classes of materials. Their historical role in the development of nations has been enormous. Land clearing, railroad and highway construction, and mining continue as important though not exclusive uses. The space program is enabled by energetic materials.

While many of the energetic materials in current use were developed in the previous century, a recent renaissance by synthetic chemists has brought forward new compounds. The response of these new materials to stimuli that cause initiation or transition from combustion to detonation and the response of energetic materials generally to a variety of new uses (such as for air bags in automobiles where the environmental conditions and longer term storage stability questions must be carefully assessed) have led to increased interest in understanding the fundamental mechanisms for initiation and decomposition and also to new methods for quality and safety assurance tests.

Understanding the sensitivity to known stimuli such as impact or heating, the routes of chemical decomposition, and the theoretical techniques that can describe these processes is a fertile field of current research addressed in this Symposium. Relations between the molecular structure and the defect structures and initiation and decomposition, properties of new materials, experimental tests and new methods for probing at the microscopic level, and theoretical progress were the main topics.

The commonality with studies of other materials using many similar experimental techniques, especially in the area of defects, and the special features of the subpicosecond time scale for reactions and decomposition both in experiments and molecular dynamics simulations provides a strong bond with other materials research. The organizers hope that these proceedings will further strengthen those bonds.

Donald H. Liebenberg
Ronald W. Armstrong
John J. Gilman

March 1993

Acknowledgments

The organizers acknowledge with thanks the efforts of Professor R. Roy and members of the Materials Research Society boards to provide a forum for the discussion of energetic materials. The support staff of MRS significantly helped this Symposium run smoothly, and encouraged the timely receipt of papers included in these proceedings. The Chairs of the Sessions are to be especially thanked for their help in the review process in addition to keeping the sessions on time and providing opportunity for stimulating discussions of the papers. These Chairs were: R. Lieb, R. Doherty, M. Berman, R. Simpson, H. Cady, W. Faust, C. Capellos, J. Oxley, J. Covino, and J. Dienes. The organizers acknowledge the support of Richard Miller and the Office of Naval Research and the response of the energetic materials community in providing an important set of papers describing current research results and future directions. We hope this Symposium has added to the breadth of materials science included in the Materials Research Society charter.

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PART I

Structure and Stability

MOLECULAR STRUCTURE AND PERFORMANCE OF HIGH EXPLOSIVES

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ABSTRACT

Empirical methods have been developed to predict density and heat of formation of proposed high explosives. These methods are parameterized in terms of molecular constituents consisting of atoms in particular bonding environments. These methods, along with the atomic composition of the molecule, are then used in an empirically based method to predict the performance of the explosive.

Together, these methods form a unified mechanism of relating molecular structure to explosive performance. Indeed, this effort, along with the synthesis effort at Los Alamos, have led to the identification of a new class of high-nitrogen molecules that may prove to be high performance explosives.

INTRODUCTION

The goal of the high explosives synthesis effort at Los Alamos has been to synthesize an organic high explosive that has the performance of HMX (one of our best performing explosives in general use) but at the same time has the insensitivity of TATB (our most insensitive high explosive). Although numerous efforts at Los Alamos, and indeed throughout the explosives community in general, have tried to achieve this goal, few new explosives have ever made been considered for weapon systems.

If we take a glance at the synthesis history of the explosives of military interest¹, we immediately see that most all of them were first synthesized in the late 1800s. The fact that synthesis efforts since this time, and particularly during the past 40 years, have not been able to realize the goal given above, was one of the reasons for the development of the methods described here.

Table I. History of the Synthesis of Explosives of Military Interest

Nitroguanidine	1877
Tetryl	1879
TNT	1880
TATB	1888
PETN	1894
RDX	1899

One common element of nearly all of the synthesis efforts during the last 40 years has been the nitration of a carbon skeleton. This has resulted in the synthesis of many polynitroaromatics, with TATB and TNT as notable examples. But, are these explosives qualitatively different from one another? To help answer this question, we developed simple empirical methods to help indicate how each molecular constituent affected an explosive's performance. In addition

to being developed as predictive tools, the primary goal of these methods is to help guide the synthesis effort by providing insight as to what constituents were beneficial to high performance and which ones were not. These methods would then complement the computer methods developed over the years in predicting properties of proposed explosives.

The empirical methods developed were concerned with density and heat of formation of the proposed explosive. Certainly, in the past, these factors have been recognized as playing an important part in the performance of an explosive. However, many synthesis efforts have had as their primary goal the synthesis of high density organic molecules instead of high performance molecules. The thought here is that the three factors of density, heat of formation, and atomic composition must all be considered when relating molecular structure to performance. Of the three factors, atomic composition has received the least emphasis.

In the sections below, we discuss the three empirical methods as related to the factors given above, and then relate them to performance.

DENSITY

One method for predicting density was developed by Stine² in 1981. This method assumed that the volume of a molecule in the unit cell of a crystal (which in this case includes some of the void volume) is a sum of the volumes of the molecular constituents. In this case, the molecular constituent is the atom in its particular bonding environment. Thus, for example, one constituent would be a carbon atom with four single bonds, designated C(1,1,1,1), or if two of the bonds were in a ring system designated C(1,1,-1,-1). Another constituent being a carbon with a double bond and two single bonds, C(2,1,1). Table II lists all of the different constituents possible for carbon, hydrogen, nitrogen, oxygen molecules, where 1, 2, or, 3 represent a single, double, or triple bond, and -5 designates an aromatic bond. A negative value indicates that the bond is part of a ring system. Values for the constituent volumes were derived from over 2000 organic molecules with known crystal structures. A histogram of the errors between the observed and calculated densities for these 2000 compounds indicates that the calculated value is within 3-4% of the observed value. Of course only a few of the 2000 compounds were explosives, but when this method was applied to over 300 organic explosives synthesized at Los Alamos, a similar standard deviation was obtained.

Of interest here are the contributions of each constituent to the density, which are also listed in Table II. It can be seen that almost all of the carbon-containing constituents contribute a relatively low value to the density, except for C(-1,-1,-1,-1) and C(1,-1,-1,-1) whose bonds are involved in multiple ring systems. That is, to be high density, the carbons must be a part of a cage-type or spiro-type structure. However, almost all of the nitrogen and oxygen atoms contribute a high value to the density. Thus for a high density compound one would want to eliminate the carbon and hydrogen atoms in favor of nitrogen and oxygen atoms.

Table II. Constituent Volumes for the Prediction of Density

Definition	Volume Å ³	Density g/cm ³
H(1) bonded to a Carbon	5.981	0.278
H(1) bonded to an aromatic Carbon	7.499	0.221
H(1) bonded to a Nitrogen	5.199	0.319
H(1) bonded to an Oxygen	0.366	4.536
C(1,1,1,1)	13.390	1.486
C(1,1,-1,-1)	11.709	1.702
C(1,-1,-1,-1)	9.755	2.042
C(-1,-1,-1,-1)	9.673	2.060
C(2,1,1)	14.565	1.368
C(1,-1,-2)	13.288	1.499
C(2,-1,-1)	12.654	1.575
C(-1,-1,-2)	10.410	1.914
C(1,-5,-5)	12.094	1.647
C(-1,-5,-5)	10.618	1.876
C(-5,-5,-5)	10.370	1.921
C(3,1) or C(2,2)	16.579	1.202
N(2,2,1)	10.368	2.242
N(1,1,1)	9.234	2.517
N(1,-1,-1)	9.798	2.372
N(-1,-1,-1)	8.759	2.654
N(-5,-5)	12.268	1.895
N(2,1)	14.488	1.605
N(-1,-2)	11.941	1.947
N(3)	15.599	1.490
O(1,1)	12.178	2.181
O(-1,-1)	12.172	2.183
O(2)	12.754	2.063

HEAT OF FORMATION

A method similar to that developed for density was developed for predicting the heat of formation of a proposed explosive³. Here, however, it is important to specify the type of atom bonded to the atom of concern. Thus, for example, a carbon bonded to two other carbons, a hydrogen, and a nitrogen would be designated by C(C1, C1, H1, N1). Also of importance to the heat of formation is the contribution of ring strain. Here we only consider ring strain in rings consisting of three, four, or five atoms. Values for the constituent heats of formation were derived from measured heats of formation of over 1100 organic compounds⁴. As opposed to similar existing methods for estimating the heat of formation of a molecule, this method has a much smaller set of constituents, and the constituent heat of formation is based on a larger set of empirical data. A histogram of the errors between the observed and calculated values indicates a standard deviation of about 10 kcal/mole.

Here again, the method indicates which molecular constituents contribute a positive amount to the overall heat of formation and which contribute a negative amount. It now becomes evident, that a particular molecular constituent might contribute in a positive way to the density, but a negative amount to the heat of formation.